



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

and combining the two,

$$\frac{L_x}{T} = - \frac{\partial(p, v)}{\partial(x, T)} \quad (13)$$

which is the generalized Clapeyron-Clausius equation. Making use of this in (11) we obtain the "well-known equation" mentioned by Professor Lewis, and given by van der Waals, p. 52:

$$\frac{\partial C_v}{\partial v} = T \frac{\partial^2 p}{\partial T^2}$$

Applying this to the case mentioned by Professor Lewis,

$$p = \varphi_1(v) + T\varphi_2(v)$$

which is the case under which van der Waals' familiar equation comes, we find, to be sure, that C_v is independent of the *volume*, but on solving for T , and writing

$$T = pV_1(v) + V_2(v)$$

and applying equations (1) and (2), we do not find anything particularly simple for C_p .

All this is very simple, but what I wish to call attention to is that in any case, the specific heats being defined by a partial differential equation of the first order, there is one perfectly arbitrary function, by no means necessarily of the temperature. In any case I believe that the teaching of thermodynamics by means of the equation of the so-called ideal gas or by means of van der Waals' equation is by no means conducive to clearness.

ANOMALOUS OSMOSE

BY F. E. BARTELL

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN*

It has repeatedly been noted that solutions of electrolytes with different types of "semi-permeable" membranes give osmotic pressure values quite different in magnitude from the calculated maximum values derived from the gas law formulations. We may define *normal osmotic pressure values* as those which conform to the gas law formulations. We have an example of this type when a solution of cane sugar is used with a semi-permeable membrane such as copper ferrocyanide. *Anomalous osmotic pressure values* are those which do not conform to the gas law formulations; they may be greater or less than the normal values. The abnormality of the effects may be of considerable magnitude and may even result in so-called negative osmose, in which case the direction of flow of liquid is from the concentrated to the more dilute solution.

* Communicated by M. Gomberg, April 20, 1920

Anomalous osmose has been observed with membranes of inorganic materials, such as unglazed porcelain¹ and finely divided metals;² with membranes of plant tissue, such as parchment paper;³ with membranes of animal tissue, such as gold beaters skin,⁴ and with membranes of organic gelatinous materials, such as gelatine and collodion.⁵ The writer has investigated each of these types of membranes and has noted their behavior when used with different types of solutions. Measurements have included osmotic pressure, the sign of the charge which exists between the membrane material and the solution, and the difference in potential which exists between the two solutions in contact with the faces of the membrane.

In order to account for abnormal osmotic effects, the following postulates have been made:

1. Capillary pores connect the two faces of an osmotic membrane. These pores become filled with liquid from the solutions bathing the membrane faces.

2. An electrical double layer may exist between the walls of the capillary pores and the liquid within them (i.e., the Helmholtz electrical layer). The magnitude of the electrical double layer depends upon the extent of the selective adsorption of the ions.

3. A difference of potential may exist between the two faces of the membrane. The magnitude of this value is primarily dependent upon diffusion, relative ionic migration velocities, and relative ionic adsorption.

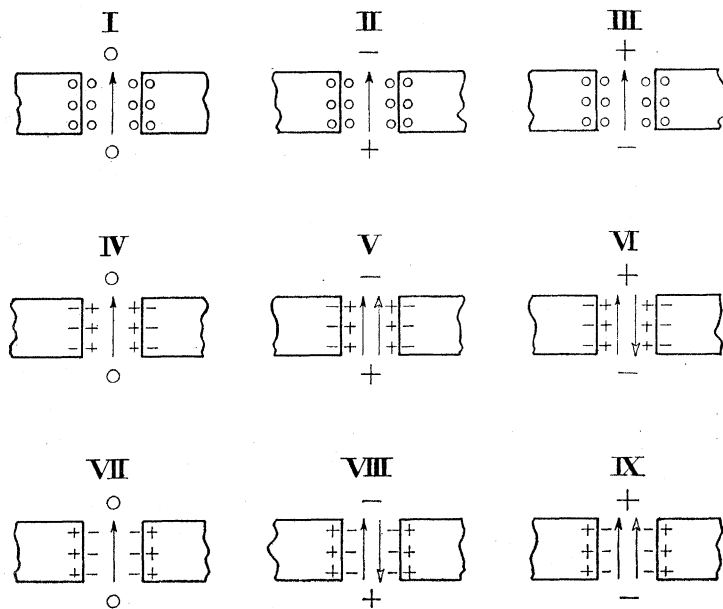
4. The forces tending to produce anomalous osmose operate in practically the same manner as do the forces in the phenomena of electrical osmose. The passage of liquid through the membrane is, in each of these cases, due to the electrical potential which is operative between the two faces of the membrane and which acts upon the charged liquid layer along the capillary wall.

5. In an osmotic system there is always operative a force tending to produce normal positive osmose. When solutions of electrolytes are used there may exist, in addition to this normal force, another force acting either with or against it, with the result that observed osmotic pressures may be either abnormally great or abnormally small.

Electrical States Which May Be Associated with the Membrane System.—According to the postulates above outlined, nine different states of electrification may exist within the osmotic system. Each of the following diagrams represents the electrical influences associated with a single pore extending through a membrane; this includes the sign of the electrostatic charge on the pore wall with the corresponding opposite charge of the liquid layer bathing this pore wall, together with the orientation of the electrical potential existing between the two faces of the membrane. The concentrated solution is in every case represented on the upper side. In each case the arrow at the left pointing upward indicates the direction of the tendency to produce normal osmose, while the arrow on the right

indicates the direction of the superimposed effect tending to produce abnormal osmose. With electrical orientations represented in cases I, II, III, IV and VII, normal osmose would be obtained; with electrical orientations represented in cases V and IX, abnormally great positive osmose would be obtained; with electrical orientations represented in cases VI and VIII, abnormally small (or negative) osmose would result.

An indication of the orientation of the electrical charge, and the magnitude of the charge, on the capillary wall system has been obtained by reducing the material of the membrane to the form of a fine suspension and then determining the electrical sign of these particles by cataphoresis, i. e., by noting the direction of movement of the fine particles when subjected to the driving force of a difference of potential.



The difference in potential between the two solutions bathing the faces of the membrane has been measured in practically all our osmotic experiments. This value has been assumed to represent the difference in potential which exists between the two faces of the membrane and to indicate at least the direction of the driving force tending to produce abnormal osmose.

It has been noted that the value of the electromotive force observed is quite different from the value calculated by assuming it to be due to contact potential. In some cases it is even opposite in sign to such calculated values.

In the following tables, the sign preceding the potential value refers to the sign of the charge on the solution side of the membrane. The (-)

sign preceding the osmose value indicates negative osmose. Some typical results are given in the following tables.

RESULTS OBTAINED WITH PORCELAIN MEMBRANE

SOLUTION	POTENTIAL OF CONCENTRATED SOLUTION SIDE	OSMOSE	SIGN OF CAP- ILLARY WALL	SIGN OF LIQUID IN CAPILLARY
0.1 <i>M</i> KNO ₃	-0.006	+64.5	-	+
0.1 LiNO ₃	+0.007	-31	-	+
0.1 Al(NO ₃) ₃	+0.310	+447	+	-
0.005 <i>M</i> HCl.....		+27		
0.01 <i>M</i> HCl.....	-0.011	+15	+	-
0.2 <i>M</i> HCl.....	+0.013	+119	+	-
0.005 <i>M</i> NaOH.....		+26		
0.01 <i>M</i> NaOH.....	-0.022	+81	-	+
0.2 <i>M</i> NaOH.....	+0.016	-45	-	+

RESULTS OBTAINED WITH GOLD BEATERS SKIN

SOLUTION	POTENTIAL OF CONCENTRATED SOLUTION SIDE	OSMOSE	SIGN OF CAP- ILLARY WALL	SIGN OF LIQUID IN CAPILLARY
0.05 <i>M</i> KCl.....	+0.002	+ 8.5	+	-
0.05 <i>M</i> LiCl.....	+0.046	+ 11	+	-
0.05 <i>M</i> AlCl ₃	+0.067	+550	+	-
0.1 HCl.....	-0.09	- 2	+	-
0.5 H ₂ SO ₄	-0.094	- 40	+	-
0.5 H ₃ PO ₄	-0.103	- 45	+	-
0.01 NaOH.....	+0.040	+ 5	-	+
0.5 NaOH.....	+0.04	- 5.5	-	+

RESULTS OBTAINED WITH POTASSIUM SALTS WITH PORCELAIN MEMBRANES

SOLUTION	POTENTIAL OF CONCENTRATED SOLUTION SIDE	OSMOSE	SIGN OF CAP- ILLARY WALL	SIGN OF LIQUID IN CAPILLARY
KCNS.....	-0.0185	+100.5	-	+
KCl.....	-0.0105	+ 80	-	+
KBr.....	-0.0090	+ 71	-	+
KNO ₃	-0.0060	+ 64.5	-	+
KI.....	-0.0050	+ 55	-	+

The results obtained show that the magnitude of the osmose varies with the magnitude of the potential. The magnitude of osmose will not vary directly with the magnitude of potential inasmuch as the electromotive force values must overcome the tendency toward positive osmose, and, also, the value of the double electric layer of the capillary wall system is different in every solution used.

Gold beaters skin in water is slightly electro-negative. Salts with univalent cations may cause the membrane material to become positively charged. The magnitude of the charge on the capillary walls increases with increase in valency of the cation. This explains the abnormally great osmose with AlCl_3 solution.

It is noted that the direction and the extent of osmose in the above experiments conform to predictions which follow from the application of the postulates given above. In those cases in which the direction of flow is not that actually indicated by the sign of the charge of the system, it will be noted that the osmose is abnormal and that the tendency is operative in the direction predicted.

The experiments with various types of membranes have been extended considerably beyond those cited. Parchment paper, gold beaters skin, collodion, and gelatine membranes have been studied. The generalizations outlined above have been found to apply very satisfactorily in the case of each of these types of membranes. The results will be published in the near future.

¹ Bartell, F. E. and Hocker, C. D., *J. Amer. Chem. Soc.*, **38**, 1916 (1036).

² Robinson, C. S., *J. Phys. Chem.*, **22**, 1918 (99); **22**, 1918 (153).

³ Unpublished data.

⁴ Girard, P., *Rev. Gen. Sci.*, **20**, 1909 (694); Lillie, R. S., *Amer. J. Physiol.*, **28**, 1911 (194).

⁵ Loeb, J., *J. Gen. Physiol.*, **2**, 1919 (87).

A PHOTOGRAPHIC METHOD OF FINDING THE INSTANTANEOUS VELOCITY OF SOUND WAVES AT POINTS NEAR THE SOURCE

By ARTHUR L. FOLEY

DEPARTMENT OF PHYSICS, INDIANA UNIVERSITY

Communicated by R. A. Millikan, April 10, 1920

Sparks from the condensers L, L (Leyden jars, charged by an electric influence machine not shown in the figure) pass across the gaps G, G, the sound gap S, and the illuminating gap I. The light from the spark at I casts a shadow (caused by refraction) of the sound wave produced by the spark at S upon the photographic dry plate P, provided the spark at I occurs at the proper time. The gaps I and S are in series, the spark at S occurring first, the spark at I being retarded the proper time interval by means of an adjustable condenser K.

D is a steel disk 76 cm. in diameter mounted to rotate at high speed just in front of and near the lower edge of the dry plate P. The rim of the disk was ground to a chisel edge and very small teeth were cut in it at intervals of a cm. or so. The intervals and teeth were made irregular